Contact Angles and Surface Tension of $Ge_{1-x}Si_x$ Melts

A. Croell[a], N. Kaiser[b], S. Cobb[c], F.R. Szofran[c], and M. Volz[c]

[a] Institut für NE-Metallurgie und Reinststoffe, University of Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany
[b] Kristallographisches Institut, University of Freiberg, Hebelstr. 23, D-79104 Freiburg, Germany
[c] SD47(now SD46), NASA Marshall Space Flight Center, Huntsville, AL 35812, USA

Introduction

Precise knowledge of material parameters is more and more important for improving crystal growth processes. Two important parameters are the surface tension and the contact (wetting) angle with a crucible, since they determine meniscus shapes in a variety of methods (e.g. CZ, EFG, FZ, detached Bridgman growth). The specific background for the experiments was twofold: a) the selection of a suitable ampoule material for the detached growth of Ge and Ge-Si alloy crystals (see papers 31a-S21-03 and 01p-K32-12) and b) the determination of the magnitude of solutocapillary convection in the FZ growth of Ge-Si crystals (see paper 31a-S14-07).

The sessile drop method allows the simultaneous determination of both surface tension and wetting angle and was used for the investigations. The samples (pure Ge as well as Ge-Si melts) were measured on different substrates between the melting temperature and 1090°C. Sapphire, fused silica, various surface treated versions of both, as well as glassy carbon, graphite, SiC, carbon-based aerogel, pBN, AlN, Si_3N_4, and CVD diamond were used as substrates. The measurements were performed either under dynamic vacuum, under argon, or under forming gas (Ar with 2%H_2). Pictures of the drops were evaluated numerically using the Young-Laplace equation. The parameters were measured for durations up to 5 days to simulate typical growth times for the alloy crystals and to detect any changes of the parameters due to slow reactions with the atmosphere or the substrate.
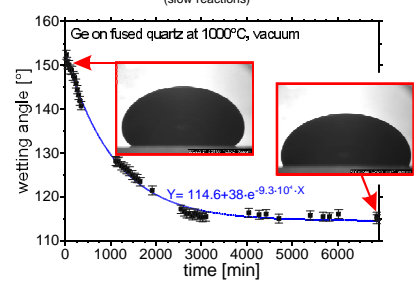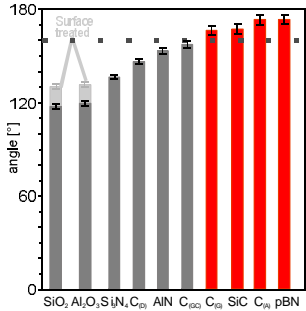
1. Sessile Drop Setup
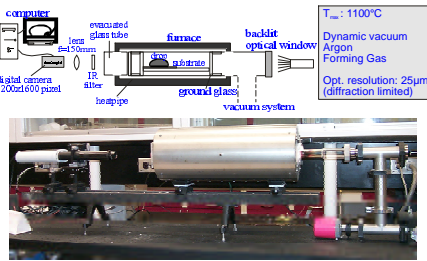
## 2. Sessile Drop Evaluation
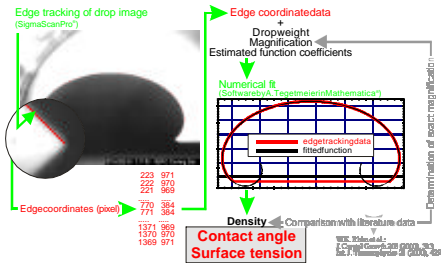
3. Long-Term Evaluation of Data
(slow reactions)

$Y = 114.6 + 38 \cdot e^{-9.3 \cdot 10^{-4} \cdot X}$

4. Results: Contact Angles for Ge

Substrate	Angle [°]
Fused quartz	150→117
Fused quartz sandblasted	155→128
Fused quartz HF fume etched	156→131
Fused quartz firepolished	148→131
Sapphire	150→119
Sapphire sandblasted	144→134
Graphite (C_G)	166±1
Glassy carbon (C_{GC})	157±2
C-based Aerogel (C_A)	173±3
C-coated fused silica	141→128
CVD Diamond (C_D)	146±1
SiC	167±3
pBN	173±3
hot pressed BN	156±2
BN layer on fused silica	144→127
AlN 3% oxides	170→157
Si_3N_4 ceramic	157→136
Si_3N_4 (CVD) on fused quartz	170→147

Contact angles >160° and no change over time: SiC, Graphite, C-based aerogel, and pBN substrates
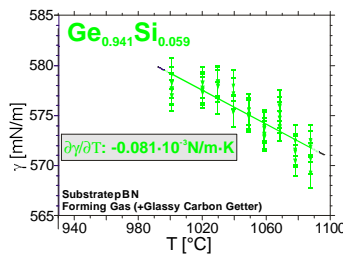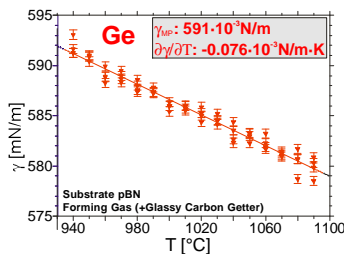
5. Results: Contact Angles for $Ge_{1-x}Si_x$
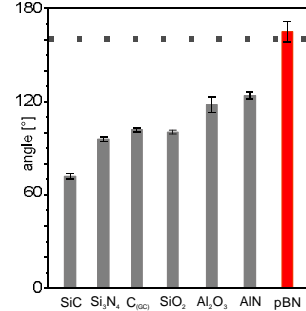
Substrate	Si [%]	Angle [°]
Fused quartz	3.3-6.6	129→100
Sapphire	4.2-4.7	126→118
Glassy carbon (C_{GC})	3.1	160→120
	4.6	149→102
SiC	6.5	165→72
pBN	2-13.4	165±7
AlN 3% oxides	6.3	168→124
Si_3N_4 ceramic	6.2	155→96
Si_3N_4 (CVD) on fused quartz	5.7	160→97
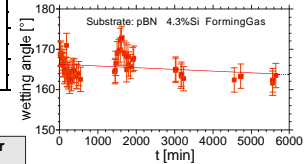
A contact angle >160° and no change over time: pBN substrates only

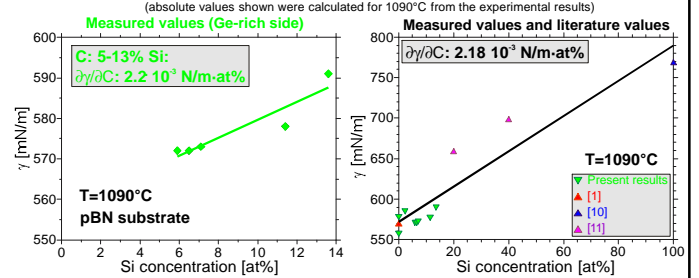## 6. Results: Temperature Dependence of Surface Tension

Ge $\gamma_{MP}: 591 \cdot 10^{-3}$ N/m $\quad \partial\gamma/\partial T: -0.076 \cdot 10^{-3}$ N/m·K

$Ge_{0.941}Si_{0.059}$ $\partial\gamma/\partial T: -0.081 \cdot 10^{-3}$ N/m·K

Substrate pBN
Forming Gas (+Glassy Carbon Getter)

Reference	γ [mN/m]	$\partial\gamma/\partial T$ [10^{-3} N/m·K]
Present results[a]	591	-0.08
[1][b]	583	-0.08
[2][c]	665	-0.08
[2][a]	590	-0.07
[3,4][d]	587	-0.105
[5]	600	-0.12
[6]	616	-0.2
[7][d], [8]	621	-0.26
[9][e]	600	-

[a] Sessile drop method
[b] Levitating drop method
[c] Ring depression technique
[d] Maximum bubble pressure method
[e] Pendant drop method

Ge: Values agree very well with recent literature data.

$Ge_{1-x}Si_x$: for x up to 0.14, the temperature dependence of the surface tension is close to that of pure Ge.

7. Results: Concentration Dependence of Surface Tension
(absolute values shown were calculated for 1090°C from the experimental results)

Measured values (Ge-rich side)

C: 5-13% Si:
$\partial\gamma/\partial C: 2.2 \cdot 10^3$ N/m·at%

T=1090°C
pBN substrate

Measured values and literature values

$\partial\gamma/\partial C: 2.18 \cdot 10^3$ N/m·at%

T=1090°C

Ge-Si on the Ge-rich side: the concentration dependence of the surface tension shows the comparatively high value of $2.2 \cdot 10^3$ N/m at%. This is in agreement with an interpolation using literature data for pure Ge and Si and intermediate Si concentrations.

In conjunction with the strong segregation in the Ge-Si system, this can be a source of solutocapillary convection in Ge-Si growth.
(See paper 31a-S14-07)

Summary

◆ For Ge melts, stable contact angles >160° were found for graphite, SiC, C-aerogel, and pBN
◆ For all oxide- and most nitride-based substrates, contact angles decreased over time
◆ For $Ge_{1-x}Si_x$ melts (x ≤ 0.14), pBN was the only substrate providing stable angles, around 165°
◆ Surface tension measurements for Ge resulted in $\gamma = 591 \cdot 10^{-3}$ N/m and a temperature coefficient of $-0.08 \cdot 10^{-3}$ N/m·K, in good agreement with recent literature data
◆ For $Ge_{1-x}Si_x$ (x ≤ 0.14), values similar to that of pure Ge were found for the temperature coefficient
◆ For the compositional dependence of the surface tension, $2.2 \cdot 10^{-3}$ N/m·at%Si was determined

References

[1] W.K.Rhim, T. Ishikawa, Int.J.Thermophysics21(2000), 429
[2] H. Nakanishi, K. Nakazato, S. Asaba, K. Abe, S. Maeda, K. Terashima, J. Crystal Growth 187 (1998) 391
[3] N. Eustathopoulos, M.G. Nicholas, and B. Drevet:Wettabilityathightemperatures. Pergamon,Amsterdam1999
[4] M. Brunet, J.C.Joud,N.EustathopoulosetP.Desre, J. of the Lesscommon Materials51(1977) 69
[5] V.M. Glazov, S.N.Chizhevskaya, N.N. Glagoleva, Liquid semiconductors, PlenumPress,New York, 1969
[6] L.B.Lazarev, TeoretcheskayaiEksperimental´nayaKhimiyaVol. 3, No.4(1967)504
[7] V. I. Davydov, Germanium,GordonandBreach,SciencePublishers,NewYork, 1966
[8] C. Allen,Thesurfacetensionofliquidmetals.,S.Z.Beer (publisher), Liquid metals;chemistryandphysics, (Dekker, NewYork,1972)
[9] P. H. Keck, W. V. Horn,Phys. Rev. 91 (1953)512
[10] W.K. Rhim and K. Ohsaka: J. CrystalGrowth208(2000),313
[11] Y. Takamura, T.Aoyama, and K. Kuribayashi: Proc.Spacebound97,Montreal1997,229